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Fatty acids fouling on forward osmosis membrane: impact of pH

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ABSTRACT

The fouling propensity of the fatty acids is investigated during the operation of the osmotically driven membrane process. Experiments were performed at various pH values ranged from 4.0 to 9.0 in the presence of the octanoic acid as the model fatty acids. Results demonstrated that the fatty acid fouling was significantly dependent on the changes of pH. In all tested pH values, permeate flux was sharply decreased during the initial coverage of fatty acids on the membrane surface, then slowly decreased as the fatty acid layer became developed. At pH 9.0, fouling propensity was less than those of pH values around 4.9 (pK_a of octanoic acid) due to the protonation of the carboxylic group of octanoic acid molecules, which resulted in electrostatic repulsion between octanoic acid molecules and membrane surfaces. The measurement of contact angle and FTIR spectra also supports that more octanoic acid molecules are adsorbed on FO membrane surfaces at the low pH than at the high pH.

Keywords: Forward osmosis; Membrane; Fatty acids; Fouling; Contact angle

1. Introduction

Forward osmosis (FO) is an osmotically driven membrane process for water production. The driving force is the concentration gradient, which enables the transportation of water from a low concentration to high concentration of salts through a selectively permeable membrane. Several researches have been reported that FO has many advantages such as high water flux, low fouling during operation as compared with reverse osmosis (RO) [1–3]. At present, FO process has been studied and applied to wastewater treatment, water quality tailoring, landfill leachate treatment, food industry, and reclamation [1,4].

Membrane fouling has been regarded as the critical barrier for the application of FO processes. Fouling on FO membrane is generated when various foulants including organic matters, particles, biocolloids, and inorganic scales are attached to the membrane surface during the filtration process. It could be elucidated the behavior formation of membrane fouling that would be formed on the membrane surface in two ways: (1) cake formation of the fouling on the membrane surface and (2) the adsorption of the fouling into the membrane structure [5]. Several researchers have reported that the performance of FO is significantly reduced with the attachment and coating of the

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membrane fouling [1,4,6]. In addition, the main mechanism in the flux decline is the adsorption and the attachment of foulants on the membrane surface leads to lower performances in desalination process including the decrease in both water flux and permeate quality [7,8].

Fatty acid is one of the main organic constituents in natural water and wastewater. The influence of fatty acid molecules has been studied in both microfiltration (MF) and ultrafiltration (UF) membranes, and the adsorption and the coating of membrane surfaces by fatty acid molecules are mainly caused the flux decline in MF and UF membrane [9–11]. Furthermore, the influence of the fatty acid molecules upon a membrane surface has been also studied, and proven as the important factor on the performance of an RO membrane [6,12]. Among various aquatic chemistries that alter the fatty acid fouling propensity, pH has been reported as the critical factor on the adsorption of fatty acids onto membrane surfaces. Brinck et al. [13] stated the fatty acid molecules reduced the flux during filtration due to the adsorption of the hydrophobic fatty acid molecules on the membrane surfaces under acidic (unadjusted) pH conditions, while did not observe the flux decline under alkaline (elevated) pH conditions. In addition, the fatty acid fouling was significant in hydrophobic membranes due to the hydrophobic interactions than in hydrophilic membranes [14]. Therefore, it is important to investigate the influence of the fatty acid on the FO membrane. However, the mechanism and behavior of fatty acid molecules at various pH values on a membrane surface have not been investigated in FO process yet.

The main objective of this research is to investigate the performance of the FO process, the behavior, and the mechanism of the flux decline at various pH values in the presence of octanoic acid molecules. The flux decline, reversal salt selectivity, and changes in surface functional groups are monitored at various pH values, and the flux decline in the presence of octanoic acid is compared with that of humic acids in the same solution chemistry.

2. Materials and methods

2.1. Preparation of FO membrane and model fatty acids

The FO membrane used in this research was kindly provided by CSM-Woongjin Chemical, Inc. (Gyeonggi-do, Korea). Before the experiment, the membrane was kept in deionized water at 4℃. Octanoic acid was selected as a model fatty acid (Junsei Chemical, Japan). The octanoic acid solution was prepared in 10 mM NaCl with 2 h of sonication and 10 h of mechanical stirring at the concentration of 50 mg/L as reported earlier [6].

2.2. FO lab-scale of the cross-flow experiment

For all experiments, the total ionic strength of the feed and draw solutions were fixed at 10 mM and 2.7 M, respectively, using NaCl. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH, when it was necessary to adjust to the experimental condition. The schematic of the lab-scale cross-flow system for the FO process is illustrated in Fig. 1. The flow rate of both draw and feed solutions was controlled by a gear pump

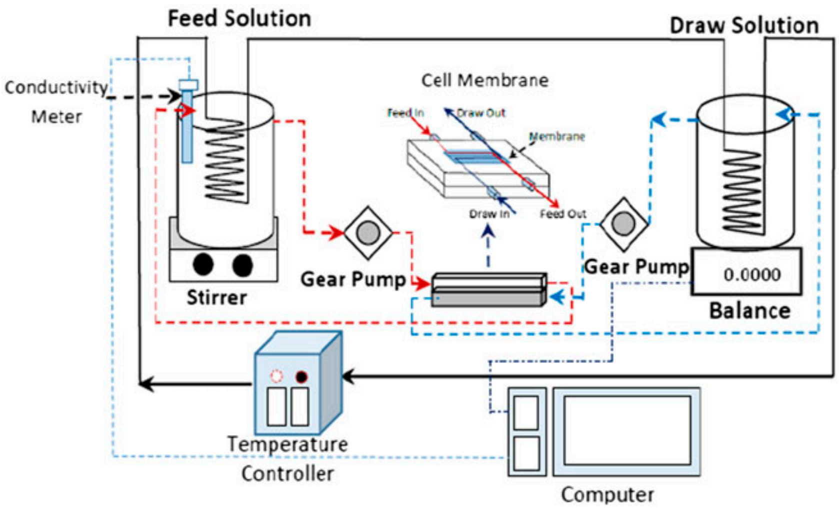

Fig. 1. Schematic diagram of the lab-scale FO setup.

(Longer Pump WT3000-1FA), and the effective area of the FO membrane was 20.0 cm^2. The mixed solutions were stirred using a magnetic stirrer to maintain well-mixed homogeneous solutions, and the change in volume of the draw solution was measured using a AND GF-4000 digital weighing scale (USA), with the values being automatically transmitted to a computer. The temperature was kept at 21 ± 0.5˚C in both feed and draw solutions by water bath (Daehan Scientific, Korea). The conductivity of feed and draw solutions, temperature, and pH were continuously monitored by data logger (LabPro, Vernier), and the desired amount of NaCl was added to the draw solution in every 480 min to keep 2.7 M of draw salt concentration.

2.3. Contact angle and FTIR analysis

Contact angles of virgin and fouled membranes were measured by contact angle goniometer (Phenix-300, USA). The sample membrane was carefully removed from the membrane cell, air-dried, and kept in storage to measure the contact angle. For the contact angle measurement, about 50 μL of deionized water was used and measurements were repeated at least five times, then averaged.

FTIR was applied to measure the adsorption of fatty acid on the membrane surface for the virgin and fouled membranes, and the obtained data were analyzed to compare the changing of the chemical functional groups on the membrane surface [12]. In this research, Spectrum One System (Perkin-Elmer, USA) was operated with the spectral range from 4,000 to 450 cm^{-1}.

2.4. Membrane fouling protocol

Initial volumes of feed and draw solutions were 4 and 2 L, respectively. Before starting the experiment, baseline of each experiment was demonstrated for 100 min with foulant-free solution (10 mM NaCl). After the flux had become stable at the initial flux of 38.0 L/m^2 h, the foulant is added into the feed solution. Fig. 2 illustrated the graphical representation of the membrane fouling protocol.

3. Results and discussion

3.1. Structure of FO membrane

The cross-section image of virgin FO membrane used in this research is shown in Fig. 3. The cross-section exhibited extremely macrovoid structure, so-called finger-like structure, below the thin and active surface layer of the membranes. The small pores at the surface decrease the wettability of the membrane and macrovoids are expected to decrease the mass transfer resistance for the faster water transport in semi-permeable membranes [15]. Hence, the membrane could get 38.0 L/m^2 h at 2.7 M NaCl as the draw solution.

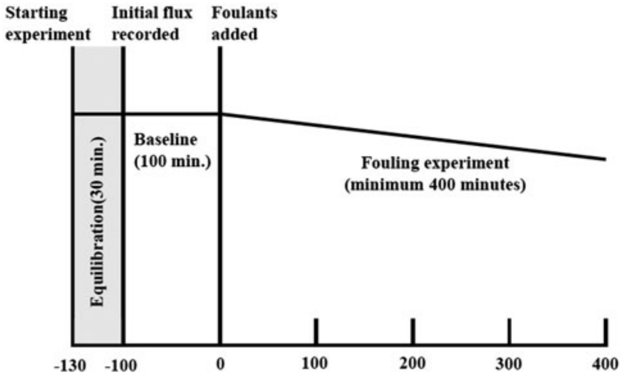

Fig. 2. Graphical representation of FO fouling experiment.

3.2. Impact of pH on the octanoic acid fouling

To understand the mechanism, behavior, and the influence of octanoic acid molecules on FO process, a pH in the feed solution was varied from 4.0 to 9.0 using 0.5 M HCl and 0.5 M NaOH with the total ionic strength of 10 mM as NaCl.

Fig. 4 illustrates the flux decline with varied pH in the feed solution in the absence and presence of 50 mg/L octanoic acid. Interestingly, initial flux dropped significantly in the presence of octanoic acid as shown in Fig. 4. This is due to the immediate adsorption of the octanoic acid molecules onto the membrane surface, rendering the hydrophilic membranes more hydrophobic, which will be further investigated in the following section. Moreover, it clearly shows that the flux decline becomes more significant when the pH decreases from 9.0 to 4.0 with 50 mg/L octanoic acid. It can be explained that the change of membrane surface charge as well as the deprotonation of octanoic acid is responsible to the different flux profiles in Fig. 4. In the monovalent ionic solution, solution pH may change the protonation of surface functional groups on polymeric membranes. Moreover, in aqueous solutions, since anions are less hydrated than cations, they can more closely approach the membrane surface. The surface will then acquire a more negative surface charge due to the presence of more anions such as Cl^- and OH^- at higher pH values [16]. In addition, at pH below the pK_a value of octanoic acid (i.e. 4.9), dissolved octanoic

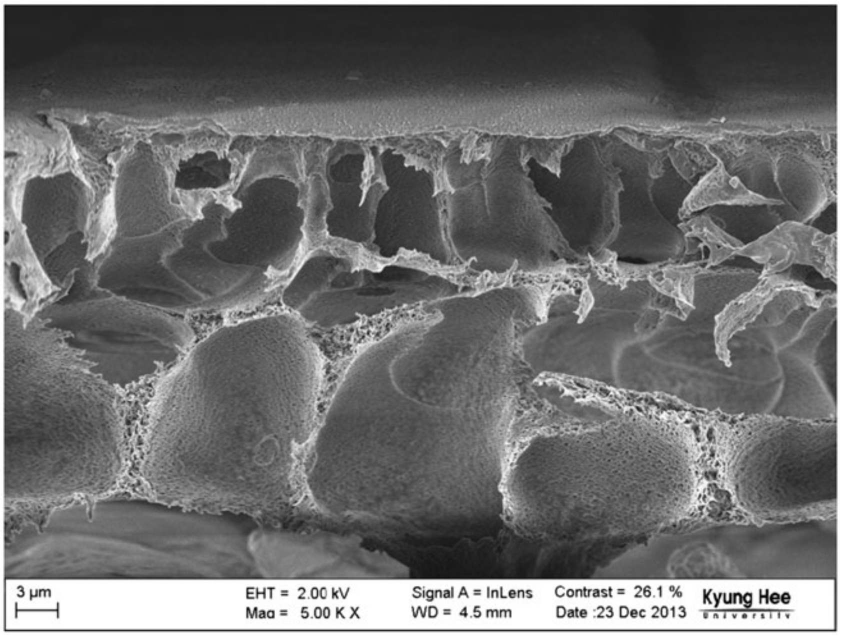

Fig. 3. SEM micrograph of the cross-section of virgin FO membrane.

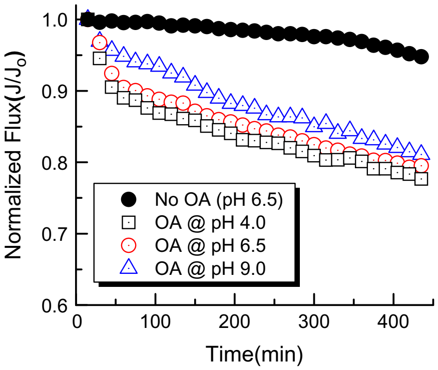

Fig. 4. Normalized flux decline at various pH values from 4.0 to 9.0 in the absence and presence of 50 mg/L octanoic acid. The initial flux (J_0) and temperature were maintained 38.0 L/m^2-h and 21 ± 0.5˚C, respectively.

acid molecules are mostly undissociated, thus behave like hydrophobic uncharged molecules [6]. At the elevated pH of the solution (i.e. 9.0), the octanoic acid molecules are fully deprotonated and act as anionic organic molecules. Consequently, at the elevated pH (i.e. pH 9.0), both the membrane surface and octanoic acid molecules are more negatively charged, which will results the increase in electrostatic repulsions between membrane surface and octanoic acid molecules. The stronger electrostatic repulsion mitigates the attachment of octanoic acid molecules and the build-up of the initial octanoic acid layer on the membrane surface. On the contrary, at low pH (i.e. 4.0), surface charge of both membrane surface and octanoic acid molecules will be decreased, thus the adsorption and build-up of the initial octanoic acid layer on the membrane surface are facilitated, and caused more flux decline than at the higher pH. The similar results that flux decline increasing with decreasing pH for octanoic acids are obtained in other studies [6,12].

After the initial drop of the flux, the flux decline is more gradually decreased with time for all tested pH values. Although the flux decline at the lower pH is more significant at the initial stage, the slopes of flux decline after the initial drops were similar in three pH values. It implies that the further build-up of the octanoic acid layer on the existing octanoic acid layer is not significantly influenced by the electrical properties of octanoic acid molecules. The trend of flux decline after the initial stage is the typical flux decline curve of formation of foulant layers on the membrane surface [17]. Consequently, it can be concluded that the flux decline at various pH values is not only related with the interaction between membrane surfaces and octanoic acid molecules, but also related with the coalescent interaction between octanoic acid molecules. The light scattering study of Ang and Elimelech [6] also supports that the aggregation of octanoic acid in aqueous solution was not significantly influenced by the pH of the solution.

3.3. Reversal salt selectivity

Reversal salt selectivity is the ratio of the volume of water produced per moles to draw solute lost [18]. The diffusions of water and draw salt molecules are attributed to the performance of the osmotically driven membrane process [19,20]. Furthermore, the reversal salt selectivity is not the function of draw solution concentration and the structure of the membrane support layer, but the selectivity of the membrane active layer is the sole parameter of the reversal salt selectivity of osmotically driven membranes [18].

To understand the impact of octanoic acid molecules on the performance of FO membrane, the reversal salt selectivity was continuously monitored at various pH values as shown in Fig. 5. The result shows that the reversal salt selectivity was slightly lower at pH 9.0 compared to pH 4.0 and pH 6.5 in the absence of OA, while there was no significant change in the presence of octanoic acid. As discussed in the previous section, the membrane surface and octanoic acid molecules are more negatively charged at the high pH (i.e. 9.0), but the influence of electrostatic interactions to the reversal salt selectivity was minimal. It might be due to the coating of octanoic acid molecules on the membrane surface. The coated layer of octanoic acid molecules plays as the barrier for the change of membrane selectivity, while the membrane selectivity was more susceptible to be changed at various pH values in the absence of octanoic acid molecules. However, it needs further investigation to clarify the changes of reversal salt selectivity with the formation of fouling layers on the FO membrane surfaces.

3.4. Changes of contact angle and FTIR spectra during octanoic acid fouling

During the operation of membrane processes, foulants will be accumulated on the membrane surfaces and they can influence membrane surface properties [1,11,21,22]. The contact angle of water droplet is the typical indicator of the hydrophobicity of a membrane surface during the operation of membrane processes. Fig. 6 illustrates the contact angle of virgin and fouled membrane with octanoic acid molecules at various pH values. It shows that contact angles of fouled membranes are always higher than that of the virgin membrane. Moreover, the contact angle of fouled membrane was highest at the pH of the solution of 4.0, followed by pH 6.5, and lowest at pH 9.0. The changes of the contact angle are attributed to the accumulation of octanoic acid molecules with different pH values and the membrane surface. Ang and Elimelech [6] also stated that the increased contact angle was due to the coating of membrane surfaces by the adsorption of organic molecules on the membrane surface. The increase in the hydrophobicity is mainly related with the amount of octanoic acid molecules on the fouled membrane. At the low pH, octanoic acid molecules are protonated and adsorbed more than at the higher pH, then behave as hydrophobic uncharged molecules. Consequently, the membrane surface becomes more hydrophobic due to the octanoic acid molecules on the membrane surface as shown in Fig. 6.

The changes of surface properties due to the adsorbed octanoic acid molecules are further investigated by FTIR. FTIR can provide the characteristic absorbance related with adsorbed octanoic acid molecules on FO membrane surface [12]. The FTIR spectra of virgin and fouled membranes are shown in Fig. 7. There were significant differences in FTIR absorbance spectra between virgin and fouled membranes in

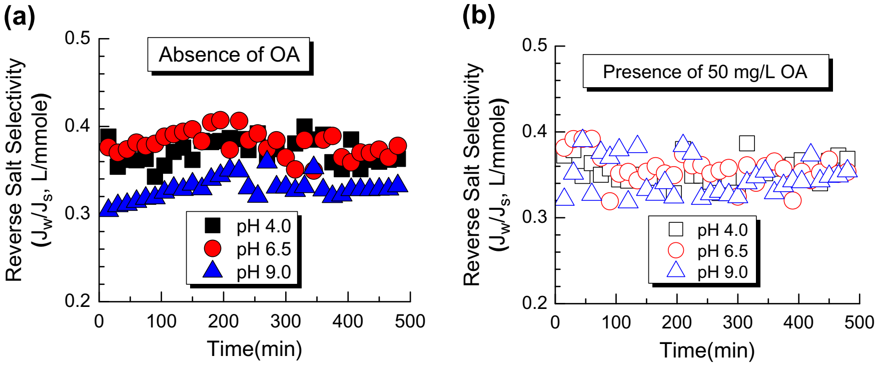

Fig. 5. Reversal salt selectivity of FO membranes: (a) in the absence of the octanoic acid and (b) in the presence of 50 mg/L octanoic acid at various pH values from 4.0 to 9.0.

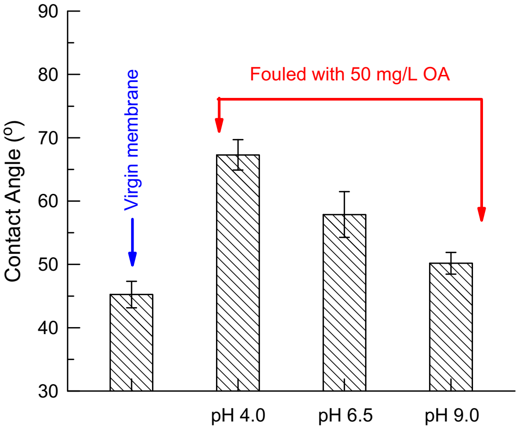

Fig. 6. Contact angle of the virgin and fouled membranes at various pH values ($n = 5$).

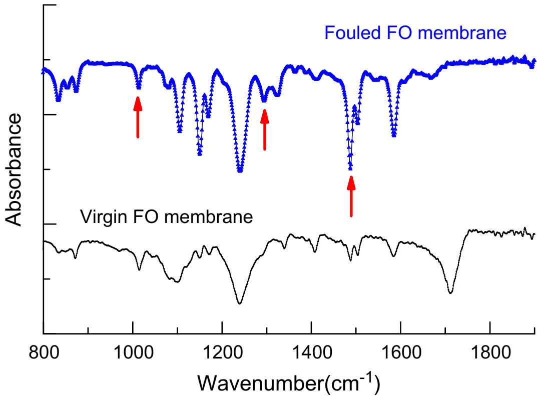

Fig. 7. FTIR spectra of virgin and fouled membranes.

the wave range from 800 to 1,800 cm^{-1}. More specifically, the absorbance at wave lengths of 950, 1,290, and 1,415 cm^{-1} is the typical footprint of octanoic acid molecules [23]. It implies that the significant amount of octanoic acid molecules is adsorbed on the fouled membrane as we expected during the fouling experiments and contact angle measurements. Consequently, it can be concluded that the fouling propensity of FO membrane process is significantly changed in the presence of fatty acids as changes of pH of the solution due to the protonation or deprotonation of functional groups in octanoic acid molecules, resulting the changes in the affinity between the membrane surface and octanoic acid molecules.

4. Conclusions

The change of pH of the solution significantly influenced to the octanoic acid fouling of FO membranes. The flux decline was more significant at low pH value of the solution (4.0) compared to high pH (9.0) due to the protonation of carboxylic functional groups in octanoic acid molecules. The adsorption of octanoic acid molecules changed the FO membrane surface became more hydrophobic and less permeable to water molecules. The measurement of contact angles and FTIR spectra for virgin and fouled membranes clearly exhibited that the main mechanism of flux decline was the initial adsorption and subsequent build-up of octanoic acid layer on the FO membrane surface. In addition, the adsorbed octanoic acid molecules did not significantly alter the selectivity of FO membrane represented as reversal salt selectivity. This result could be attributed to the significant contribution of the organic fatty acids remained in wastewater effluent to the fouling of FO process during the wastewater reuse.

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